30

MAGNETIC STUDIES ON MOLYBDENITE

By AJIT KUMAR DUTTA

ABSTRACT. A method for determining the principal magnetic susceptibility in a particular direction of the crystal where the balancing method is not suitable has been developed. The magnetic anisotropy and the principal susceptibilities of molybdenite have been measured. The anisotropy is discussed with the known structure of the crystal.

INTRODUCTION

According to the modern theories of semiconductors (Wilson, 1931, 1932, 1939) the appreciable electrical conductivity exhibited by these crystals at ordinary temperatures is due either to electrons in a nearly empty energy band, or to "holes" in a band nearly filled with electrons. These electrons are furnished by impurity centres in the crystal whence they are thermally excited into the lowest empty band of allowed levels, where these are free to move through the lattice. While the mobile "holes" are likewise created in a nearly full band by electrons being raised from that band to the vacant energy levels which may be present in the impurity atoms, these impurities being due to the stoichiometric excess of one of the constituent elements in the crystal over the other. The former class of semi-conductors are known as "excess conductors," and the latter as "defect conductors." Experimentally this classification is generally effected by the measurement of the Hall Coefficient,—"excess conductors" having negative and "defect conductors" having positive Hall Coefficients. Molybdenite has been found to have a negative Hall effect which means that the current in it is mainly carried by electrons. If, however, the distribution of these electrons deviates from a spherical one, modern ideas of diamagnetism suggest the presence of a directed diamagnetic effect towards the normal to the plane of motion of these few conduction electrons. The only magnetic measurement on molybdenite that has been reported, is by Tjabbes (1932), that too being with powders of molybdenite, thereby supplying no clue to our above conjecture.

From the above considerations it is evident that the study of the magnetic properties of single crystals of molybdenite will be of considerable interest. The present paper gives an account of these measurements made at room temperatures. The measurement of the magnetic properties of molybdenite at temperatures other than the room temperature, both high and low, the Hall effect and other important allied properties are in progress and will be published in due course.

MEASUREMENT OF THE MAGNETIC ANISOTROPY OF MOLYBDENITE

The magnetic anisotropy was measured by the torsional method adopted by Krishnan and his collaborators (1935). The crystal is suspended with its

basal plane vertical in a uniform magnetic field at the end of a fine calibrated quartz-fibre, the other end of which is attached to a graduated torsion head. The crystal tends to bring its basal plane to parallelism with the field, showing that the specific susceptibility of the crystal along directions in the basal plane, say χ_1, is greater (algebraically) than that along the vertical axis, χ_{II}. The torsion head is suitably rotated, so that in the natural setting position of the crystal, when the field is on, the torsion of the fibre is zero. The torsion head is then slowly rotated until the equilibrium is just unstable; this is the position of maximum couple. If this angle is denoted by α, the difference in maximum and minimum susceptibilities in the horizontal plane of suspension is given by (Banerjee and Bhattacharyya, 1928)

$$C(\alpha-\psi)=\frac{1m}{2M}\cdot H^2(\chi_1-\chi_{II})\sin 2\psi \qquad \ldots \quad (1)$$

where ψ is the angle of rotation of the crystal, C is the torsional constant of the fibre, M and m are the molecular weight and mass of the crystal respectively and H is the field strength. The strength of the magnetic field and the dimension of the fibre are so adjusted that the angle through which the torsion head is rotated to bring the crystal from the intial position corresponding to zero torsion to that corresponding to the maximum couple, always attains a value more than 360 degrees so that the approximate formula

$$\chi_1-\chi_{II}=\frac{(2\alpha-\pi/2)MC}{mH^2} \qquad \ldots \quad (2)$$

holds true. By rotating the torsion head in both clockwise and anticlockwise directions, α can be accurately determined and therefore $\chi_1-\chi_{II}$.

Since the crystal is a naturally occurring one and in view of the uncertainty regarding the impurities present in the crystal obtained from different sources, the measurements were repeated with a number of specially chosen single crystals. The values of $\chi_1-\chi_{II}$ obtained in these measurements were found to be slightly different for different crystals as will be seen in Table I.

MEASUREMENT OF THE PRINCIPAL SUSCEPTIBILITIES

After completing the measurement of $\chi_1-\chi_{II}$, if we can determine the absolute value of either χ_1 or χ_{II}, both of them will be known. Since χ_1 is numerically smaller than χ_{II}, it is desirable to choose χ_1 for this measurement.

On trial the balancing method of Krishnan (*loc. cit.*) for measuring the absolute susceptibility has been found to be unsuitable in the determination of χ_1. This is due to the fact that the volume susceptibility of molybdenite in that direction is greater than that of any of the solutions ordinarily used. So the method has been modified as follows.

The crystal is attached with its basal plane vertical to one end of a stout glass rod of suitable length, the other end being attached to the middle of a fine silver wire stretched horizontally between a graduated torsion head and a metal chuck. By rotating the torsion head small lateral displacements can be imparted

to the crystal. The whole arrangement is so placed that the crystal is about 4 to 5 mm away from the vertical sides of the flat polepieces and so in a non-homogeneous magnetic field, the gradient being in the horizontal direction. The attachment of the molybdenite crystal to the end of the glass rod is effected in such a way that its basal plane is always parallel to the direction of the uniform part of the field. To be sufficiently ensured that the horizontal gradient of the field is only effective in laterally displacing the crystal, the silver wire

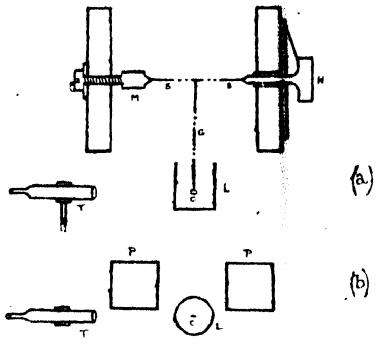

FIG. 1

(*a*) Vertical Section (*b*) Horizontal Section
M—Metal chuck SS—Silver wire
H—Torsion head G—Glass rod
L—Liquid bath T—Telemicroscope
PP—Pole pieces C—Crystal.

is always kept sufficiently stretched. The entire arrangement is suitably encased to prevent it from dust and wind. Fig. 1 represents diagrammatically the different parts of the arrangement.

For measuring the susceptibility, the crystal is kept suspended in a liquid of known volume susceptiblity, say K_1, and viewed through a telemicroscope, one of whose scale marks is made coincident with an edge of the crystal. When the field is switched on the crystal moves laterally along the gradient in a direction away from the field. The torsion head is then slowly rotated until the crystal returns to its original position. Let θ_1 be the angle through which the torsion head has been rotated. If K_c be the volume susceptibility of the crystal, the force displacing it away from the field is given by

$$\tfrac{1}{2}AHx\frac{dHx}{dx}(K_c-K_1)$$

where A is the cross-section of the crystal and H is the field strength, the horizontal direction being taken to be the x-direction. This force has been balanced by the torsion of the silver wire. Therefore

$$\tfrac{1}{2}AHx\frac{dHx}{dx}(K_c-K_1)=R\theta_1 \qquad \ldots \quad (3)$$

where R is the torsional constant of the wire. The liquid is then replaced by another liquid having a different volume susceptibility, say K_2, and the whole procedure is repeated. If θ_2 be the corresponding angle through which the torsion head has been rotated, then

$$\tfrac{1}{2}AH_x\frac{dH_x}{dx}(K_c-K_2)=R\theta_2.$$

The gradient remains the same in both the cases, the crystal being brought to the same position every time; so from (3) and (4) we have

$$\frac{K_c-K_1}{K_c-K_2}=\frac{\theta_1}{\theta_2} \qquad \ldots \quad (5)$$

and hence K_c can be easily calculated. The density of the crystal being known, the mass susceptibility is easily determined. In our case this corresponds to χ_1.

In our actual experiment the liquids used were conductivity water and a standard Nickel chloride solution. Measurements were repeated with a number of crystals obtained from different samples. The values of susceptibilities were found to differ slightly from crystal to crystal as will be seen from Table I.

RESULTS

The experimental results are given in Table I, where measurements on crystals from five different samples of molybdenite are shown. Here χ_{II} represents the susceptibility along the hexagonal axis and χ_I that at right angles to the axis, while χ represents the mean, susceptibility, *i.e.*, $\chi=(2\chi_I+\chi_{II}/3)$, and the corresponding volume susceptibility being denoted by K. All the above quantities are expressed in E. M. C. G. S. units. The data in the table refers to measurements taken near about 30°C.

TABLE I

Crystal	$(\chi_I-\chi_{II})\times10^{-6}$ per gm. mol.	Volume susceptibility $K\times10^{-6}$	Density	Corresponding $\chi_I\times10^{-6}$ per gm. mol.	Mean $(\chi_I-\chi_{II})\times10^{-6}$ per gm. mol.	Mean $\chi_I\times10^{-6}$ per gm. mol.	Mean susceptibility $\bar{\chi}=\frac{2\chi_I+\chi_{II}}{3}$ per gm. mol.
1	42.4	−1.243	4.804	−41.4			
2	42.5	−1.360	4.782	−45.5			
3	41.3	−1.435	4.854	−47 3	42.8	−44.3	−58 6
4	44.4	−1.293	4.926	−42.0			
5	43.3	−1.404	4.949	−45.4			

DISCUSSIONS

Molybdenite crystal belongs to the hexagonal system and has a perfect basal cleavage. It occurs in nature in the form of thin flakes parallel to the basal plane. Its structure has been determined by Pauling and Dickinson (1923) and Hassel (1924). They found that the X-ray diffraction photographs agreed with a typical hexagonal layer lattice. Each sulphur atom is equidistant from three molybdenum atoms, and each molybdenum atom is surrounded by six equidistant sulphur atoms at the corners of a trigonal prism of altitude 3.17A and edge 3.15A. The atoms in the crystal are so situated that all the trigonal prismatic units are oriented parallel to one another, the hexagonal axis being perpendicular to the triangular faces of the prism. Each layer of the crystal consists of three planes,—one of molybdenum atoms surrounded on either side by a plane of an equal number of sulphur atoms; two layers of sulphur atoms are contiguous. The distance from the molybdenum atom to the nearest sulphur atoms has been calculated to be 2.41A, which is exactly equal to the sum of the radii of molybdenum and sulphur atoms, *i.e.*, 1.36A and 1.05A respectively and the interatomic distances in the planes of a layer being 3.15A. But the distance between two such parallel layers is 3.66A. This great distance between the layers is undoubtedly connected with the excellent basal cleavage of molybdenite.

The structure of molybdenite having a trigonal prismatic configuration, arrived at by the X-ray methods has been puzzling various workers due to a belief prevalent formerly that the Mo—S bond should be ionic in character, in which case the octahedral arrangement would be more stable. Moreover the large number of its octahedral complexes containing electron pair bonds would also suggest an octahedral electron pair bond structure. But it has been found by Hultgren (1932) from a wave mechanical treatment, that in this case six equivalent bonds of strength 2.983 (considerably higher than that of octahedral bond eigenfuctions) directed towards the corners of a trigonal prism can be formed. The theoretical ratio of altitude to base of the prism should be unity while that obtained experimentally is 1.007, confirming the trigonal prismatic orientation.

From the above structural considerations of the crystal it is evident that the atoms in it are held together by different types of bindings. The three planes, one of molybdenum having two sulphur planes on either side of it are bound into a compact layer of the crystal by forces that are undoubtedly of the type that arises out of covalency (as evidenced from the above discussions) and form a gigantic two dimensional molecule. These molecules are then held together largely, presumably by Van der Waal's forces. But on looking into the interatomic distances in the different planes of the layers, it is very difficult to ascertain the exact type of binding between them. Goldschmidt (1929) on the discussions of the structures of metallic disulphides observed that the appearance of layer lattices seems to depend upon whether the metal is able to

ionise with four electrons and thereby split the molecule S_2. Therefore, metals with high valency and large radii may give rise to layer lattices, while pyrites type of lattices are restricted to metals with low valencies and small radii. Thus from his considerations it is clear that the bindings between the atoms in the planes composing the layers, may be thought to be of partially ionic in character. Certain properties of molybdenite such as electrical conductivity (different in different directions), metallic lustre, resistance to mechanical and thermal treatment photo-conductivity and etc. also suggest that the presence of binding of a slightly metallic type in the planes does not seem to be quite improbable.

One consequence of such a type of binding in the planes, will be an amount of enhanced diamagnetism in a direction perpendicular to the planes. That is exactly what has been observed in our case. Whereas the susceptibility along directions in the basal plane is -44.3×10^{-6} per gm. mol., that along the hexagonal axis is about -87.1×10^{-6} per gm. mol., *i.e.*, the anisotropy is about 72 per cent.

From the considerations of Hultgren and others (*loc. cit.*), it is found that strong d-s-p bonds are formed between Mo and S. Therefore, strong crystalline electric fields arising out of this covalency is sufficient to quench the orbital magnetic moments. Kimball (1940) has shown that in MoS_2 having trigonal prismatic orientation, d^4sp bonds are formed with Mo. Again Mo being quadrivalent in molybdenite (Pauling, 1939) two electrons are left which can be accommodated in the one 4d orbital left after bond formation. According to Pauli's principle, the spins of the electrons in that orbital, being antiparallel, balance one another. Thus no paramagnetic effect is possible from the spin or orbital moments. However, there might be a contribution of the orbital moment's high frequency elements, in which case the susceptibility, according to Van Vleck (1932), is given by

$$\chi = -\frac{Le^2}{6mc^2}\sum r^2 + \frac{3}{2}\sum\frac{|m^0(n';n)|^2}{h\nu(n';n)} \text{ per gm. mol.} \quad \ldots (6)$$

where $m^0(n';n)$ is an element of the electronic angular momentum matrix corresponding to transition frequency $\nu(n';n)$. The material is diamagnetic or paramagnetic depending upon whether the first or second term of (6) is greater. After deducting the diamagnetic contribution of sulphur as determined by Nilakantan (1936) molybdenum is found to be diamagnetic. If, however, we take into account the diamagnetic contribution from the molybdenum atom, which has been calculated according to the method of Slater (1930) as modified by Angus (1932), molybdenum is found to be still diamagnetic which contradicts the suggestion put forward by Roychowdhury and Sengupta (1936) that molybdenum will be paramagnetic in MoS_2 after correcting for the diamagnetism of molybdenum atom. Thus our experimental finding is quite in agreement with the above theoretical discussions, the high frequency paramagnetism being practically evanescent in this case.

In conclusion, the author wishes to express his best thanks to Prof. K. Banerjee, D.Sc., F.N.I., F.I.A.S., for his keen interest in the work and to Mr. A. Mookherji, M.Sc., for helpul discussions.

INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE
210, BOWBAZAR STREET, CALCUTTA.

REFERENCES

Angus, W. R., 1932, *Proc. Roy. Soc.*, **A.**, **136**, 569
Banerjee, K. and Bhattacharyya, J., 1938, *Zeits. f. Krist.*, **100**, 420.
Goldschmidt, V. M., 1929, *Trans. Farad. Soc.*, **25**, 278.
Hassel, O., 1924, *Zeits. f. Krist.*, **61**, 92.
Hultgren, R., 1932, *Phys. Rev.*, **40**, 891.
Kimball, G. E., 1940, *Jour. Chem. Phys.*, **8**, 188.
Krishnan, K. S. and Banerjee, S., 1935, *Phil. Trans.*, **A.**, **234**, 265.
Nilakantan, P., 1936, *Proc. Ind. Acad. Sci.*, **A.**, **4**, 419.
Pauling, L. and Dickinson, R. G., 1923, *Jour. Am. Chem. Soc.*, **45**, 1466.
Raychowdhury, D. P. and Sengupta, P. N., 1936, *Ind. Jour. Phys.*, **10**, 253.
Slater, J. C., 1930, *Phys. Rev.*, **36**, 57.
Tjabbes, B. Th., 1932, *Proc. Roy. Acad. Amstdam*, **35**, 693.
Van Vleck, J. H., 1932, *The Theory of Electric and Magnetic Susceptibilities*, 275.
Wilson, A. H., 1931, *Proc. Roy. Soc.*, **A.**, **133**, 458.
,, ,, 1932, *Proc. Roy. Soc.*, **A.**, **134**, 277.
,, ,, 1939, *Semiconductors and Metals.*